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COLLABORATIVE RESEARCH AND DEVELOPMENT (CR&D)

Delivery Order 0065: Nanostructured Dynamic Modulus Materials

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14. ABSTRACT
This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at Wright-Patterson AFB, Ohio from 2 November 2006 through 1 March 2008. This task worked to develop hybrid, potentially nanostructured materials that exhibit novel mechanical damping and tunable modulus. The preparation, characterization, and fundamental understanding of new, high-performance shape memory materials helps address Air Force needs relevant to the development of everything from next-generation actuators to self-deploying structures or morphing airframes. In particular, porous shape-memory thermosets hold significant promise as a class of shape-memory materials due to their ability to accommodate large amounts of elastic strain and release significant mechanical work in a controlled fashion. The goal of this work was to prepare porous shape memory thermosets via the solution-gelation (sol-gel) technique, to form hybrids of these materials with high-Tg open-cell foams so as to enhance shape memory characteristics, and to develop new means of quantifying the shape memory properties of these materials.

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Summary

A thermoset block copolyurethane (PCL/PTMO) of similar structure to the Morthane™ TPU (which displays T_c based shape memory) previously investigated by the group of R. Vaia (AFRL/MLBP) was formulated and a search routine developed utilizing 3-D Hansen solubility space to allow for the production of porous xerogels via the sol-gel technique. While these porous PCL/PTMO systems did not demonstrate the shape memory properties of the original Morthane thermoplastic due to the suppression of crystallinity following sol-gel processing, this work nevertheless demonstrates the development of a guided protocol by which porosity may be achieved via the sol-gel process using an arbitrary thermosetting formulation – an important achievement with respect to future efforts. In addition, a family of porous semi-aromatic thermoset polyesters was explored; while improvements in reaction control are still in progress, this family of materials has nevertheless demonstrated significant T_g based shape-memory in addition to good thermal and mechanical stability. With respect to characterization methods, a simple, portable high-temperature compression test fixture was designed and constructed and its utility for large-scale, high-stress testing demonstrated in a convection oven, while a series of novel DMA protocols were developed to more precisely quantify shape memory in smaller samples. Finally, as a first step towards modeling these materials, a functional 1D COMSOL transient thermal model incorporating a phase transition has been developed. In addition to expanding our knowledge base in this area, all of these results are distinct from what is found in the literature, and publications are anticipated as a result of this work.

INTRODUCTION

This report summarizes our efforts to develop, characterize and understand thermoset shape memory polymer using solution gelation chemistry, with multiple new techniques developed to create porosity in such systems. All materials produced in the course of this work were characterized by TGA (ThermoGravimetric Analysis) and DSC (Differential Scanning Calorimetry), with additional testing techniques and equipment developed as necessary. In parallel, a transient thermal model of the shape-memory activation process has been developed. Each polymer family and each technique will be described separately in the following pages.

Synthesis of Porous PCL/PTMO Block Copolyurethane Thermosets ("Morthane™ equivalent")
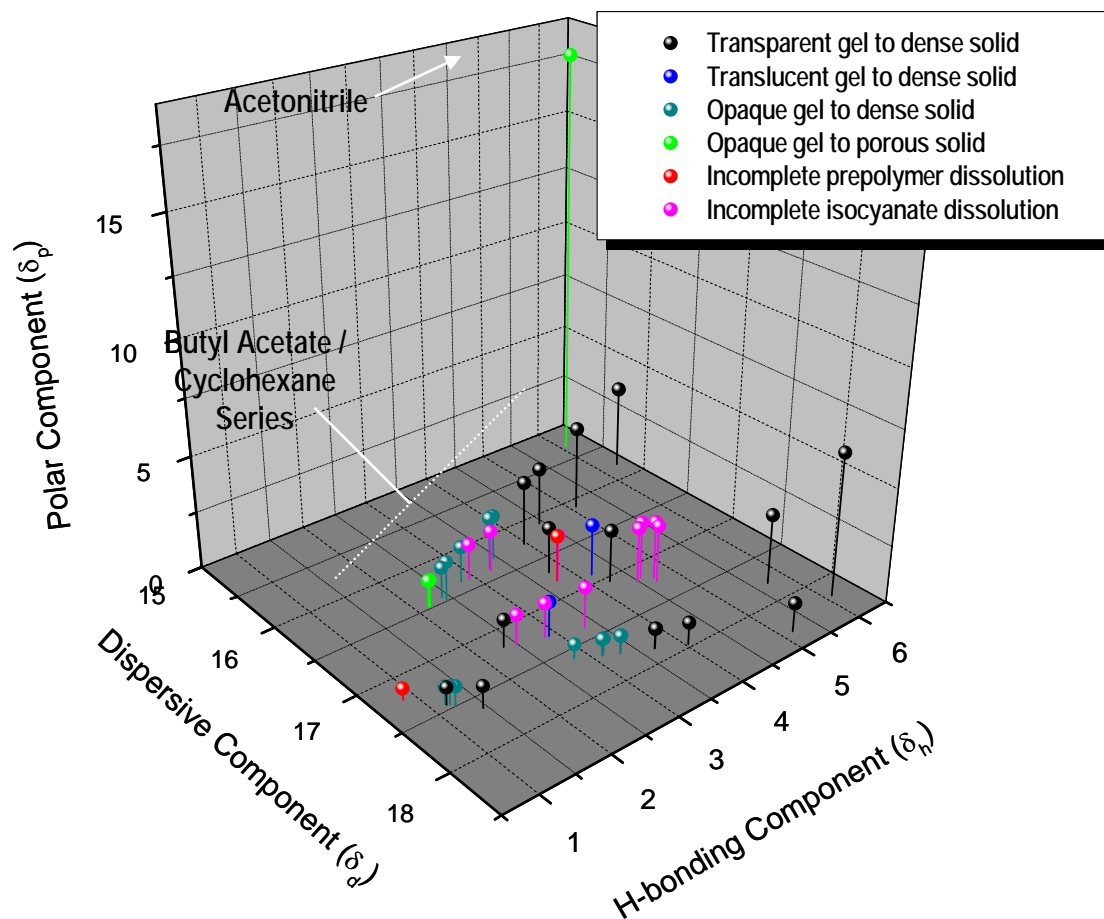
The initial step in this project was to prepare a (porous) thermoset version of the shape memory copolyurethane Morthane™ via organic sol-gel chemistry. The development of porosity in these systems required the development of a search routine optimized to minimize trial and error and identify the right solvation conditions in a logical, systematic fashion. Following the success of this approach, porous xerogels were tested for shape memory using a compression fixture developed for this work. While some recovery was observed during the first heating cycle following programming, this effect was not repeatable through later cycles and appears to have been related to chemical changes in the network as a result of heat and pressure. Nevertheless, this work demonstrates the utility of the compression test fixture, as well as the method of identifying solvation conditions appropriate for the generation of porous networks given an arbitrary formulation (a technique that has been successfully applied to other systems).

Analysis of the published structure and molecular weight data on Morthane™ led to a sol-gel chemistry formulation based on an equimolar combination of polycaprolactone (PCL) diol ($M_n \sim 1250$) and a poly(tetramethylene ether) glycol (PTMO) ($M_n \sim 1000$), reacted with

triphenylmethane-4,4',4''-triisocyanate (Desmodur RE™), a crosslinker highly analogous to the diphenylmethane-4,4'-diisocyanate (MDI) used to prepare Morthane™, in a range of solvents including ethyl & butyl acetate, tetrahydrofuran, 1,4-dioxane, acetone, 2-butanone, cyclohexane and acetonitrile.

A combination of soluble fraction and swelling data obtained from fully dense samples coupled with the Hansen solubility parameters of the solvents in question was used as a guide for finding the right solvent or a mixture of solvents to use to create a porous sample. ASTM 2765 test method C is used as the model for solvent swelling and extraction. Initial gel samples that were not porous were used in a multi-solvent swelling and extraction test. The solvents used were: tetrahydrofuran, 1,4-dioxane, acetone, 2-butanone, ethyl acetate, butyl acetate, chloroform, toluene, *o*-xylene, cyclohexane, n-hexane, n-pentane, acetonitrile, and methylcyclohexane. To make porous xerogels required comparison of two methods of ranking the solvents. The first comparison is based on the ratio of the soluble fraction to the volume swell measured in a given solvent. The second comparison involves a solvent's ranking (vs. the other solvents used) in terms of volume swell and soluble fraction. Based on the idea that the prepolymers must dissolve but the growing network must phase separate in order to generate porosity, those solvents with a high soluble fraction (indicating good compatibility with the prepolymer) coupled with a low degree of volume swell (indicating minimal compatibility with the final network) were considered to be the best candidates for creating a porous xerogel.

The highest ranked solvents are then used to create gels which are observed for their porosity. Typically these systems operate near the solubility limits of the prepolymers or the diisocyanate, meaning the solvent volume in the solutions of the two must be adjusted to ensure full dissolution prior to mixing. Mixtures of solvents are then used to shift the system in 3-D Hansen solubility parameter space towards regions where porosity is expected based on the results of the initial screening in combination with the aforementioned solvent selection criteria. In this way, porous sol-gel PCL/PTMO block copolyurethanes were created both by using acetonitrile and by using a blend of cyclohexane and butyl acetate. A three-dimensional plot showing the locations of a number of these systems in 3-D Hansen solubility parameter space is shown below.

Polar Component (δ_p)

Dispersive Component (δ_d)

H-bonding Component (δ_h)

Acetonitrile

Butyl Acetate /
Cyclohexane
Series

- ● Transparent gel to dense solid
- ● Translucent gel to dense solid
- ● Opaque gel to dense solid
- ● Opaque gel to porous solid
- ● Incomplete prepolymer dissolution
- ● Incomplete isocyanate dissolution

An additional method for creating porosity uses a solvent that can be readily frozen and maintained in the solid state, such as cyclohexane (MP = 6.5 °C) or 1,4-dioxane (MP = 11.8 °C). The gelling solution is immersed in liquid nitrogen to quickly freeze it, then stored in a freezer to allow the gelation of the remaining prepolymer and crosslinker, now highly concentrated in the interstices between solvent ice crystals. In contrast, simple freezing in liquid nitrogen following gelation does not produce sustainable porosity. While the successful application of this technique requires precise knowledge of the gel time of the formulation, it offers a means to add directionality to the pore structure, thus expanding the range of structures accessible via the sol-gel method.

Development of a High-Temperature Compression Test Fixture

Initial shape-memory testing was based on various existing ASTM standards for rubber & urethane creep testing and informed by nickel-titanium shape-memory testing including D926, D6049, D575, D1621 with input from D6515, D3768 and F2082. A special test fixture was designed and built to meet the anticipated compression test requirements, and was used to test cylindrical porous xerogels (d ~ 2-3 cm, h ~ 1 cm) and smaller, non-porous xerogels. The strengths of this approach are the ability to perform high-stress testing with large numbers of samples under a variety of conditions through the construction of multiple fixtures, all of which may be placed in the same oven. The disadvantages of this fixture are its lack of precision and the necessity for fairly large samples. As such, complimentary DMA testing techniques were

also developed to more precisely quantify shape memory in both compression and tension with smaller amounts of material

Key Features

- Accepts up to 3" diameter samples

- Designed to operate at up to 250 °C

- Screw-mounted contact plates are readily replaced (shown are glass-fiber reinforced Teflon contact plates, aluminum also available)

- Integrated steel ruler for height measurements

- Red high temperature silicone coated lead weights of 1/8" (~100g), 1/16" (~50g), and ¼" (~200g) thickness allow a range of compression forces up to 5 kgf
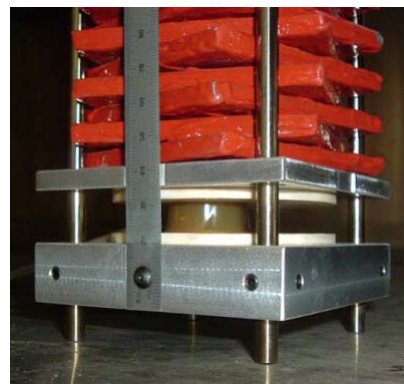
Synthesis of Porous Semi-aromatic Polyester Thermosets

A series of porous, fully amorphous polyester systems based on hyperbranched aliphatic polyester polyols (Boltorn™ H20, H30 & H40) reacted with terephthaloyl chloride or adipoyl chloride in a variety of solvents were previously reported by other members of Schmidt group[1]. While some of these materials were found to be appropriate for tissue engineering applications, others, including the more thermally and physically robust semi-aromatic systems, showed a lack of cytocompatibility but were nevertheless observed to reversibly soften upon exposure to boiling water – hinting at the possibility of (T_g-based) shape memory behavior. With that said, the formation of these gels was found to be almost instantaneous when sufficient amounts of TEA (triethylamine) were used to consume all HCl evolved during the course of the polymerization, making reproducibility and structural homogeneity difficult to achieve. A more in-depth exploration of these initial observations resulted in the formation of a porous shape memory material based on Boltorn™ H40 reacted with terephthaloyl chloride and 1% of the amount of TEA necessary to neutralize the HCl produced. In DMA testing this polymer demonstrated compression shape memory with repeatable strain recovery of 27% when unconstrained and the ability to perform up to 1.1 MPa·% of work during recovery (maximized at 0.481 MPa imposed stress which yielded 11.4% strain recovery). The DMA-based testing method detailed below has been developed in compression testing and extended to tension testing in order to characterize a range of materials (thin strips and dense cylinders) based on this formulation.

Development of a DMA Shape Memory Test Method

DMA (Dynamic Mechanical Analysis) is very well suited to quantifying shape memory (SM). SM testing requires precise control of the temperature and force a sample experiences through a complex series of events while continuously measuring stress and strain. The basic SM cycle consists of two stages: A programming stage that defines a temporary shape, and a release

[1] Poonam Borgaonkar, Sachin Sharma, Ming Chen, Sankha Bhowmick, Daniel F. Schmidt; A Flexible Approach to the Preparation of Polymer Scaffolds for Tissue Engineering; Macromolecular Bioscience,Volume 7, Issue 2 , Pages 201 – 207 , Special Issue: Bioinspired Materials . Published Online**:** 13 Feb 2007

stage that restores the material to its original shape. During both cycles the temperature and stress (force) imposed on the sample must be controlled and the sample's strain response must be measured. The TA DMA Q800 used in this work can impose forces up to 18 N in magnitude while measuring absolute dimensions to 0.1 µm and controlling temperature to 0.001 °C. The use of a small cylindrical sample in combination with a compression fixture allows for the testing of compression shape memory. The use of a thin strip of sample in combination with a film tension fixture allows both simple tensile testing and the testing of tensile shape memory.

The programming stage of the SM cycle requires three basic steps. First, the sample must be warmed above the glass transition (T_g) or crystalline melting (T_m) temperature. The new shape is then imposed on the sample through the application of sufficient force to give rise to a particular displacement. Based on our work, it is critical at this point that the material be given time to complete the programming step based on the kinetics of the phase transformation in question and the viscoelastic response of the sample. Finally, the temporary shape is set or locked in by cooling the sample below the glass transition (T_g) or crystallization (T_c) temperature while under load, again taking into account the speed with which the material undergoes the appropriate thermal transition under the imposed stress state. The temperatures for the low and high ends of the cycle are chosen based on DSC data indicating T_c / T_m and / or T_g onset / completion.

The goal of the SM release stage is to measure the stress and strain during the recovery of the sample to its initial shape as a function of temperature. While some imposed stress is necessary during recovery simply to allow the DMA to continue to track the dimensions of the sample, this stage may be performed under near-zero imposed stress in order to determine the maximum extent of recovery. In addition, progressively higher stresses may be imposed during the recovery process in order to quantify the amount of work the material is capable of doing, and the relationship between applied load and degree of recovery. As above, the importance of giving the sample sufficient time to react to changes in temperature and applied force cannot be overemphasized.
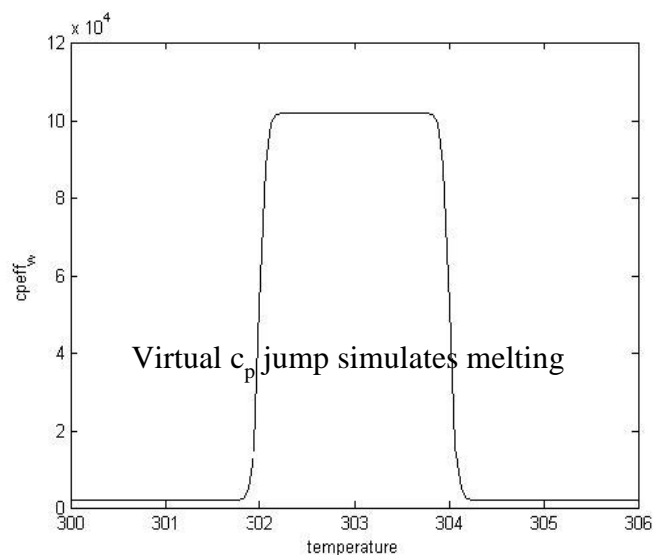
Transient Thermal Model

A transient thermal model is under development in COMSOL, a package chosen for its versatility, ease of use and availability on campus. COMSOL Multiphysics™[2] is an extendable simulation environment containing 1, 2, and 3 dimensional modeling interfaces, an automatic finite element meshing program and an extensible set of applicable mathematical models and iterative solution engines. It comes with a transient thermal analysis engine that allows the specification of all properties and interfaces to be simulated, and is extensible with subprograms written in MATLAB™ style code[3].

Currently we have running a 1D transient thermal analysis model using experimentally determined heat capacity (c_p) and thermal conductivity (k) data, either from the literature or from DSC measurements of the materials produced in this work. The model includes a simulation of a crystalline melting transition that uses the melting energy, the melting temperature (T_m) and has

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[2] http://www.comsol.com/products/multiphysics/

[3] http://www.mathworks.com/products/pfo/

Virtual c_p jump simulates melting

an adjustable range of temperatures over which melting should occur. This model of T_m changes the c_p as a function of the temperature as shown in the adjacent graph (next page). It uses a smoothed Heaviside function available in COMSOL to create smooth transitions so as to ensure convergence of the COMSOL solver.

The 1D model is a reasonable approximation of thin films being shape-memory tested in tension in the dynamic mechanical analysis (DMA) equipment. The model can be compared to a material's thermal behavior in the DMA where the external temperature can be measured and the shape memory behavior indicates the internal temperature. The remaining unknowns for modeling the test conditions are the boundary condition heat transfer coefficients (h) in the DMA. Future work will attempt to extend this model to T_g based systems, with more dimensions added as needed.

Conclusions

Two new families of porous thermosets were successfully developed, produced, and characterized, using a series of novel synthetic and analytical methods and protocols, developed specifically for the purposes of this work. The methods developed to create porosity using solution-gelation chemistry and to test shape memory expand on our ability to broadly pursue the stated goals of this work. The DMA test methods developed were successfully used to quantify the shape-memory recovery work of a promising semi-aromatic polyester system, demonstrating both the properties of this material and the capabilities of this method. The utilization of photolatent bases to allow for improved reaction control and the combination of this system with Basotect™ open-cell foam in order to boost its shape memory capabilities are underway. Finally, the synthetic and analytical methods developed here are being extended to and validated using additional families of polymers, and ongoing modeling efforts are bringing us closer to the ability to describe the behavior of these systems based on readily measurable materials properties.

ASTM Test Standards as a source of test methods and sample sizes
for shape memory polymers (SMP).

A review of ASTM standards suggests that sample sizes for compression and recovery testing

Procedures for testing recovery in rubbers, urethanes and shape memory nickel-titanium alloys were reviewed for useful sample sizes and test methods for SMPs.

	Recovery:		
	Compression	**Bend**	**Shape Memory**
Std.	**D926**	**D 6515**	**F 2082**
Sample size	cylinder 16 mm in diameter and 10 mm in height	3* 100 ± 0.5 by 10 ± 0.05 by 2.0 ± 0.2 mm	
Force			
Std.	**D6049**	**D 3768 Urethanes**	
Sample size	diameter of 30.0 ± 0.1 mm height of 13.0 ± 0.1 mm (0.51 ± 0.004 in.)	4 mm thickness, 25 mm width by 150 mm in length	
Force			
Std.	**D575**		
Sample size	28.6 ± 0.1 mm (1.129 ± 0.005 in.) in diameter (650 mm$_2$ (1.000 in.$_2$) in area) and 12.5 ± 0.5 mm (0.49 ± 0.02 in.) in thickness		
Force	Apply the force to produce a deflection rate of 12 ± 3 mm/min (0.5 ± 0.1 in./min)		
Std.	**D1621 Rigid Cellular Plastics**		
Sample size	5 specimens; square or circular in cross section with a minimum of 25.8 cm$_2$ [4 in.$_2$] and maximum of 232 cm$_2$ [36 in.$_2$] in area. The minimum height shall be 25.4 mm [1 in.] and the maximum height shall be no greater than the width or diameter of the specimen.		
Force			

What equipment
e.g. *D 3768: Flexural Recovery Test Fixture,*
D 926 parallel plate plastometer,
D 575 & D 1621 instrumented compression test (universal test machine)

ASTM D 926 – 04 Standard Test Method for Rubber Property—Plasticity and Recovery (Parallel Plate Method)
ISO 2007 and D 3194 use a similar principle
parallel plate plastometer (w 5Kg compression platen)
sample size and shape
3. Summary of Test Method
3.1 *Plasticity*:
3.1.1 A specimen of specific volume and height is tested at room temperature or heated to a specified test temperature for 15 min and then subjected to a compressive force of 49 N for a specified time.
3.1.2 At the end of this time, the height of the specimen is measured, and the plasticity number is calculated.
3.2 *Recovery*—There are two recovery procedures.

3.2.1 *Procedure A*—The test specimen is removed from the plastometer immediately after the determination of plasticity and allowed to cool and recover some of its original height for 1 min. The height is measured again and the recovery is calculated.

3.2.2 *Procedure B*—The test specimen is compressed to a height of 5 mm for 30 s and then allowed to recover at the test temperature for 5 min. The height is measured again and the recovery is calculated.

-Recover measurement apparatus and methodology described in Practice D 3767, Procedure A,

-test temperature shall be 23 (room temperature), 40, 70, 85, or 100°C

7. Test Specimens

7.1 The specimen shall be a right cylinder 2.00 ± 0.02 cm3 in volume and be free from air pockets. (A cylinder 16 mm in diameter and 10 mm in height is appropriate.) The specimen may be prepared from either a solid piece or plied sheets of unvulcanized rubber approximately 1.5 mm in thickness, care being taken to exclude air pockets in the sheet. The specimens may be cut from the sheet either by means of two mating dies conforming to Fig. 2, which produce cylinders of the correct volume, or a rotating die having an internal diameter of approximately 16 mm. If a rotating die is used, the height of the cylinder shall be adjusted until the volume is 2.00 ± 0.02 cm3. If the density is known, weighing may be used to adjust to the correct volume. If necessary, the specimen shall be placed in a suitable holder so that it is not appreciably deformed before testing.

ASTM D 3768 – 06 Standard Test Method for Microcellular Urethanes—Flexural Recovery

Flexural Recovery Test Fixture

sample size and shape

The recommended standard test specimen is 4 mm in thickness, and the minimum specimen thickness shall not be less than 3 mm. The specimen shall be 25 mm in width by 150 mm in length [1 by 6 in.].

Procedure

7.1 There shall be at least three recovery measurements.

7.2 Measure the thickness of specimen to the nearest 0.03 mm.

7.3 Insert the test specimen in the lower slot of the specimen clamp and position the end of the specimen flush with the rear face of the bend mandrel. Tighten the clamp while holding the specimen in a horizontal position. (Do not allow the outer end of the specimen to be in contact with the base of the test fixture.) A spacer of approximately the same thickness as the test specimen must be used in the upper slot to ensure proper clamping in the lower slot. A specimen mounted in a test fixture at the start of a test is shown in Fig. 2.

7.4 Make an initial reading where the mandrel edge of the specimen (the surface of the test specimen that is in contact with the bend mandrel) intercepts the protractor scale. Make a reading to the nearest 1° and record the value.

7.5 Apply force approximately 30 mm [1.25 in.] from the clamp and bend the specimen 180° around the mandrel. Hold the specimen for 5 ± 1 s in the bent position, then release slowly and allow to recover. Start the timer immediately upon release. Do not allow the specimen to drag on the fixture base during recovery. A specimen that is being bent 180° around the mandrel is shown in Fig. 3.

7.6 Read the intercept of the mandrel edge of the specimen on the protractor scale after 30-s and 300-s recovery. The difference between these readings and the initial reading is the appropriate flexural recovery value in degrees.

ASTM D 575 – 91 (2001) Standard Test Methods for Rubber Properties in Compression

instrumented compression test (universal test machine)

sample size and shape

Summary of Test Methods

3.1 These tests constitute one kind of compression stiffness measurement. Deflection is the change in thickness of the specimen upon application of a compressive force. The two different procedures are as follows:

3.1.1 *Test Method A—Compression Test of Specified Deflection*—A compression test in which the force required to cause a specified deflection is determined.

3.1.2 *Test Method B—Compression Test at Specified Force*—A compression test in which the specified mass or compressive force is placed on the specimen and the resulting deflection is measured and recorded.

NOTE 1—Comparable results are obtained only when tests are made on specimens of exactly the same size and shape, tested to the same percentage deflection, or tested under the same force.

6.2 Standard test specimens shall be 28.6 ± 0.1 mm (1.129 ± 0.005 in.) in diameter (650 mm2 (1.000 in.2) in area) and 12.5 ± 0.5 mm (0.49 ± 0.02 in.) in thickness, from which all molded surface layers have been removed.

ASTM D 1621 – 04a Standard Test Method for Compressive Properties Of Rigid Cellular Plastics

instrumented compression test (universal test machine)

sample size and shape

6.1 The test specimen shall be square or circular in cross section with a minimum of 25.8 cm2 [4 in.2] and maximum of 232 cm2 [36 in.2] in area. The minimum height shall be 25.4 mm [1 in.] and the maximum height shall be no greater than the width or diameter of the specimen. Care should be taken so that the loaded ends of the specimen are parallel to each other and perpendicular to the sides.

NOTE 2—Cellular plastics are not ideal materials, and the compressive modulus may appear significantly different, depending on the test conditions, particularly the test thickness. All data that are to be compared should be obtained using common test conditions.

6.2 All surfaces of the specimen shall be free from large visible flaws or imperfections.

6.3 If the material is suspected to be anisotropic, the direction of the compressive loading must be specified relative to the suspected direction of anisotropy.

6.4 A minimum of five specimens shall be tested for each sample. Specimens that fail at some obvious flaw should be discarded and retests made, unless such flaws constitute a variable the effect of which is desired to study.

ASTM D 3489 – 06 Standard Test Methods for Microcellular Urethane Materials

3.1.1 *microcellular urethane*—an elastomeric material made by the interaction of a polyol and an organic isocyanate, having cell diameters in the range from 0.0001 to 0.001 mm, with a minimum density of 160 kg/m3[10 lb/ft3].

5. Sampling

5.1 Test samples can be made in any suitable mold. The following three sizes are recommended (length, width, and thickness): 305 by 152 by 3.15 mm [12 by 6 by $\frac{1}{8}$ in.], 305 by 152 by 6.3 mm [12 by 6 by $\frac{1}{4}$ in.], and 305 by 152 by 12.5 mm [12 by 6 by $\frac{1}{2}$ in.].

5.2 The procedure used to prepare the test sample relating to component ratios, temperature, mixing direction, mold temperature, and curing conditions shall conform to the manufacturer's recommendations.

5.3 The test sample shall be allowed to age a minimum of 48 h before testing, at 23 ± 2°C [73.4 ± 3.6°F] and 50 ± 5 % relative humidity.

10. Compression Set

10.1 Determine the compression set in accordance with Test Methods D 395, Method B, using 22 h at 70°C [158°F]. Cut the specimen from the 12.5-mm [0.5-in.] sample, retaining the molded surfaces.

11. Compression Deflection

11.1 Determine the compression deflection at 25 % deflection in accordance with Test Methods D 575. Cut the specimen from the 12.5-mm [0.5-in.] sample, retaining the molded surfaces. The sample is not preflexed. The initial compression value is reported.

12. Resilience

12.1 Determine the resilience by vertical rebound test in accordance with Test Method D 2632. Cut the specimen from the 12.5-mm [0.5-in.] sample, retaining the molded surfaces.

19. Flexural Modulus

19.1 Determine flexural modulus, using the general procedure in Test Methods D 790, Method I.

19.2 The following test parameters are recommended for microcellular urethanes:

19.2.1 *Specimen Size*—Length 75 ± 0.5 mm [3.0 ± 0.02 in.], width 25 ± 0.5 mm [1.0 ± 0.02 in.], and thickness 3.2 ± 0.2 mm [0.125 ± 0.01 in.].

19.2.2 *Span*—50 mm [2.0 in.].

19.2.3 *Rate of Crosshead Motion*—0.20 ±0.02 mm/s [0.5 in./min].

19.2.4 *Calculation*—Calculate the tangent modulus of elasticity. See 11.11.1 of Test Methods D 790.

NOTE 3—When calculating slope, use the steepest tangent as shown in Fig. 1.

NOTE 4—The crosshead rate of 0.2 mm/s [0.5 in./min] differs from the rate of 0.02 mm/s [0.05 in./min] specified in Test Methods D 790. Test data have shown that the faster rate provides a lower coefficient of variation than does the slower rate.

19.2.5 Condition a specimen at the test temperature for a minimum of 30 min.

21. Flexural Recovery

21.1 Determine the flexural recovery of microcellular urethane in accordance with Test Method D 3768.

D 6515 – 00 (Reapproved 2004) Standard Test Method for Rubber Shaft Seals Determination of Recovery From Bending

This seems to be a practical test for measuring bending set at a temperature in flat samples:
thickness of 2.0 ± 0.2 mm (0.080 ± 0.05 in.) of each compound to be evaluated, prepared according to the procedure detailed in Practice 3183. Test sheets shall be vulcanized according to the same conditions of time and temperature as would be used for molding the sheets for testing physical properties in tension (see Test Method D 412).
7.2 After the test sheets have been conditioned for at least 16 h at 23°C (73.4°F), prepare three 100 ± 0.5 by 10 ± 0.05 by 2.0 ± 0.2 mm (3.937 ± 0.02 by 0.393 ± 0.002 by 0.080 ±0.008 in.) specimens for each material to be evaluated. Specimens shall be cut parallel to the mill grain direction.

D 6049 – 03 Standard Test Method for Rubber Property—Measurement of the Viscous and Elastic Behavior of Unvulcanized Raw Rubbers and Rubber Compounds by Compression Between Parallel Plates

D 5459 – 95 (Reapproved 2001) Standard Test Method for Machine Direction Elastic Recovery and Permanent Deformation and Stress Retention of Stretch Wrap Film

18. Specimen Preparation

8.1 Cut five strips parallel to the machine direction that are 1.0 in. (25.4 mm) wide and long enough to provide for an initial grip separation of 5 in. (127 mm).

8.2 Measure the thickness of each specimen at five equally spaced points in the area that will be between the grips to the nearest 0.001 in. (0.003 mm) and record the values.

D 6049 – 03 Standard Test Method for Rubber Property—Measurement of the Viscous and Elastic Behavior of Unvulcanized Raw Rubbers and Rubber Compounds by Compression Between Parallel Plates1
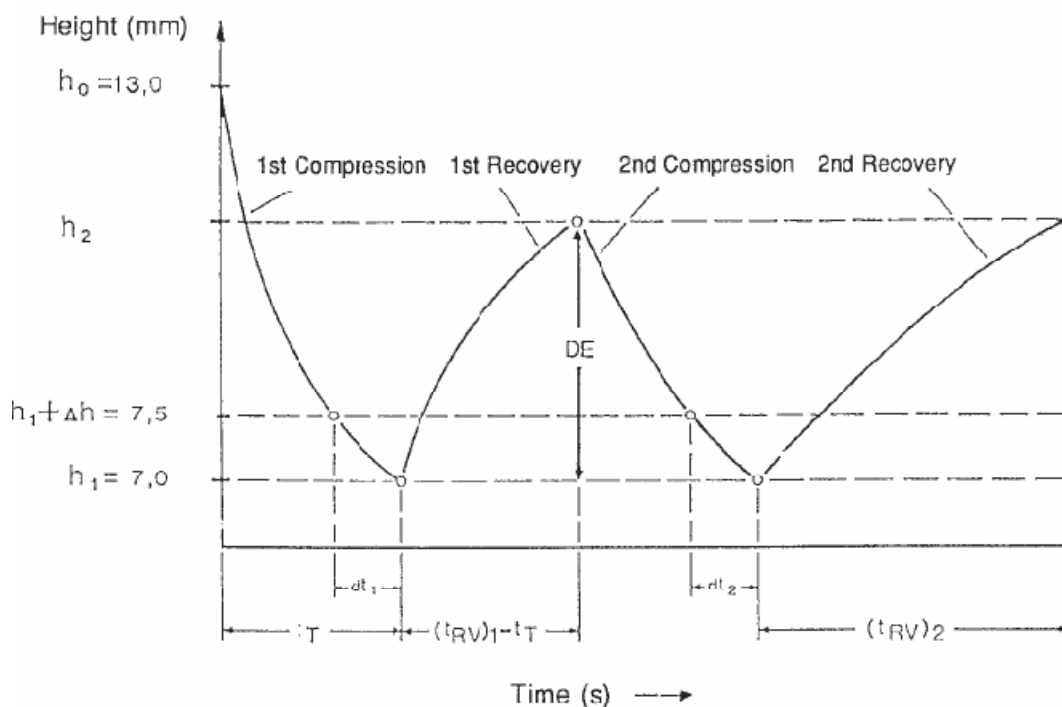
3.1.1.3 *elasticity number, DE30*—the elastic recovery expressed in units of 0.1 mm (0.004 in.) calculated from the height h_2 of the test piece after compression from 13.0 to 7.0 mm (0.51 in. to 0.28 in.) within 30 s followed by a recovery period of 30 s.

7. Apparatus [5]

7.1 *Compression Device*:

7.1.1 Two circular platens with a diameter of 30.0 ± 0.1 mm (1.181 ± 0.004 in.) and a thickness of at least 2 mm (0.08 in.) mounted in an angle iron frame, are facing each other horizontally. The upper platen can be vertically

moved and raised at least 14 mm (0.55 in.) above the lower platen to permit insertion of the 13-mm (0.51-in.) high test piece.

7.1.2 The upper platen shall be able to move nearly without friction, that is, it must smoothly descend under the contact force specified in 7.1.5.

7.1.3 The upper platen shall be capable of applying a compressive force between 1 and 800 N (0.22 and 180 lbf) ± 0.5 % to the test piece within 1 s. The force should be applied rapidly but not abruptly.

7.1.4 After the height of the test piece has been reduced from 13.0 to 7.0 mm (0.51 to 0.28 in.) the compression force shall be released in less than 0.5 s.

7.1.5 A residual compression force of 0.040 ± 0.005 N (0.009 ± 0.001 lbf) shall always be maintained by the upper platen to warrant an intimate contact with the test piece prior to compression and during the recovery cycle. The mass of the upper platen must be taken into account and compensated for.

7.1.6 The position of the upper platen shall be continuously recorded during the test to the nearest 0.01 mm (0.0004 in.) in at least 0.05 s intervals. The starting time of the compression cycle, the time of reaching compression heights of 7.5 and 7.0 mm (0.30 and 0.28 in.), and the recovery times shall be recorded to the nearest 0.05 s.

7.1.7 The compressed test pieces shall only be in contact with the two platens and the platens shall be kept free of contamination. The test piece arrangement is illustrated in Fig. 1.

8.1 The cylindrical test piece shall have a height of 13.0 ± 0.1 mm (0.51 ± 0.004 in.) and a diameter of 30.0 ± 0.1 mm (1.18 ± 0.004 in.).

Nitinol testing:

F 2082 – 06 Standard Test Method for Determination of Transformation Temperature of Nickel-Titanium Shape Memory Alloys by Bend and Free Recovery

3.2 *free recovery*—unconstrained motion of a shape memory alloy upon heating and transformation to austenite after deformation in a lower temperature phase.

4. Summary of Test Method

4.1 This test method involves cooling a test specimen to its nominally fully martensitic phase, deforming the specimen, and heating the specimen to its fully austenitic phase. During heating, the motion of the specimen is measured and plotted versus the specimen temperature. For a two-stage transformation, the R'_s, R'_f, A_s, and A_f, as defined in Terminology F 2005, are determined. For a single-stage transformation, the A_s and A_f are determined.

9.2 Select a mandrel according to the sample diameter or thickness to give an outer fiber strain of 2 to 2.5 %. For these strains, mandrel diameter shall be between 39 and 49 times specimen diameter or thickness.

9.3 Cut a test specimen long enough to wrap 90 to 180° around the mandrel.
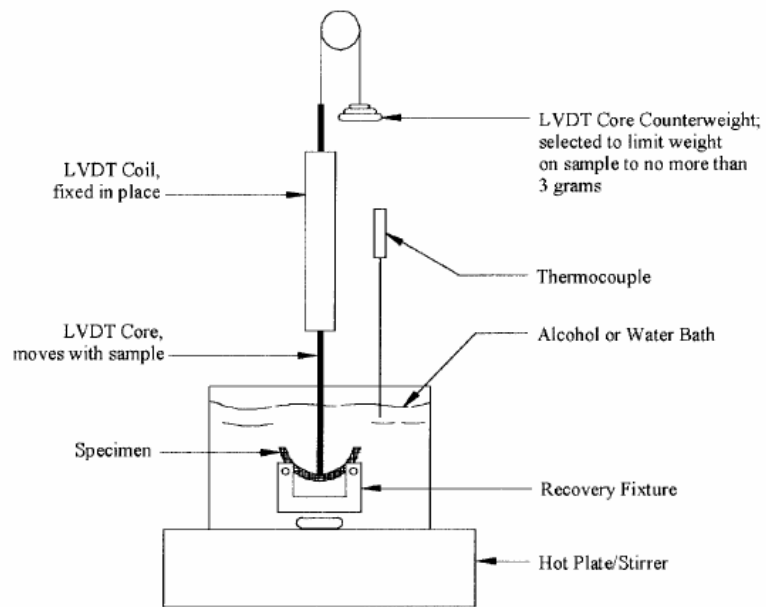
FIG. 1 Schematic Showing Side View of Test Apparatus Using a Vertically Mounted and Counterbalanced LVDT (LVDT Power Supply, Thermocouple Indicator, and Data Acquisition System Are Not Shown)
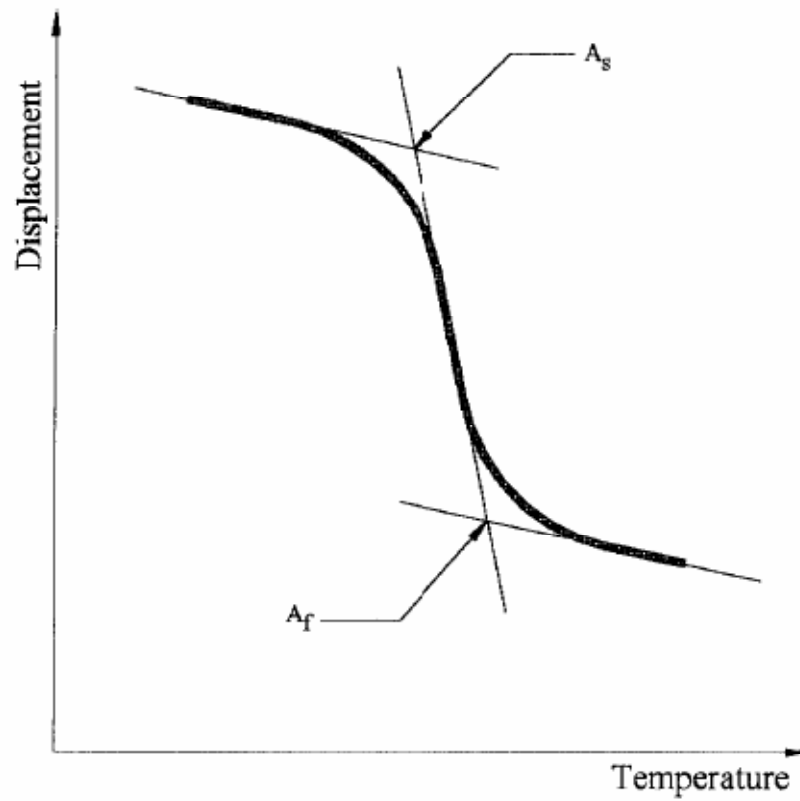
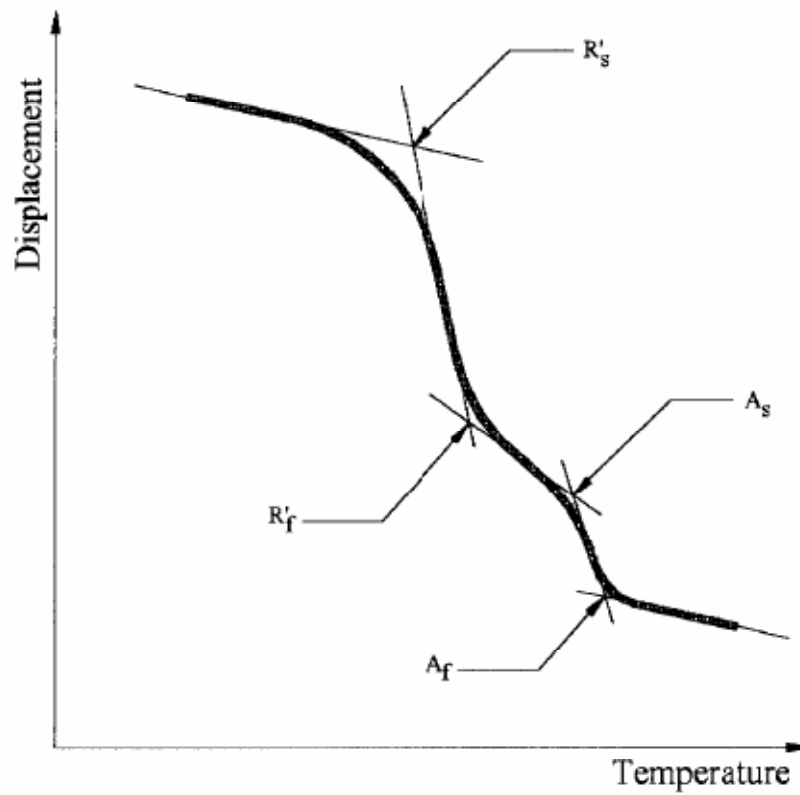FIG. 5 One-Stage Transformation—Tangent Lines and Transformation Temperatures

FIG. 6 Two-Stage Transformation—Tangent Lines and Transformation Temperatures

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F 2063 – 05 Standard Specification for Wrought Nickel-Titanium Shape Memory Alloys for Medical Devices and Surgical Implants

F 2005 – 05 Standard Terminology for Nickel-Titanium Shape Memory Alloys

austenite, *n*—the high temperature parent phase in Ni-Ti shape memory alloys with a B2 crystal structure. This phase transforms to R-phase or martensite, or both, on cooling.

austenite finish temperature (*Af*)**,** *n*—the temperature at which the martensite to austenite transformation is completed on heating in a single-stage transformation (Fig. 1) or the temperature at which the R-phase to austenite transformation is completed on heating in a two-stage transformation (Fig. 2).

austenite peak temperature (*Ap*)**,** *n*—the temperature of the endothermic peak position on the differential scanning calorimeter (DSC) curve upon heating for the martensite to austenite transformation in a single-stage transformation (Fig. 1) or the temperature of the endothermic peak position on the DSC curve upon heating for the R-phase to austenite transformation in a two-stage transformation (Fig. 2).

austenite start temperature (*As*)**,** *n*—the temperature at which the martensite to austenite transformation begins on heating in a single-stage transformation (Fig. 1) or the temperature at which the R-phase to austenite transformation begins on heating in a two-stage transformation (Fig. 2).

bend and free recovery (BFR), *n*—a test method for determining austenite transformation temperatures on heating.

DISCUSSION—The test involves cooling a wire or tube specimen below the Mf temperature, deforming the specimen in a controlled fashion, then heating through the austenite transformation. By measuring the shape memory response of the specimen As and Af, temperatures can be determined. This test method is covered in Test Method F 2082.

R-phase, *n*—the intermediate phase which may form between austenite and martensite.

DISCUSSION—This occurs in Ni-Ti shape memory alloys under certain conditions. The crystal lattice of the R-Phase is a rhombohedral distortion of the cubic austenite crystal lattice structure, hence the name "R-phase."

R-phase finish temperature (Rf), *n*—the temperature at which the transformation from austenite to R-phase is completed on cooling in a two-stage transformation (Fig. 2).

R-phase peak temperature (Rp), *n*—the temperature of the exothermic peak position on the DSC curve upon cooling for the austenite to R-phase transformation (Fig. 2).

R-phase start temperature (Rs), *n*—the temperature at which the transformation from austenite to R-phase begins on cooling in a two-stage transformation (Fig. 2).

R*-phase finish temperature (R*f), *n*—the temperature at which the martensite to R-phase transformation is completed on heating in a two-stage transformation (Fig. 2).

R*-phase peak temperature (R*p), *n*—the temperature of the endothermic peak position on the DSC curve upon heating, for the martensite to R-phase transformation in a two-stage transformation (Fig. 2).

R*-phase start temperature (R*s), *n*—temperature at which the martensite to R-phase transformation begins on heating in a two-stage transformation (Fig. 2).

residual elongation (Elr[%]), *n*—the strain after tensile loading to 6 % strain and unloading to 7 MPa.